

April 29, 1880.

THE TREASURER in the Chair.

The Presents received were laid on the table, and thanks ordered for them.

The following Papers were read:—

I. "Note on the Spectrum of Carbon." By J. NORMAN
LOCKYER, F.R.S. Received April 8, 1880,

In the year 1878* I communicated to the Royal Society a paper in which the conclusion was drawn that the vapour of carbon was present in the solar atmosphere.

This conclusion was founded upon the reversal in the solar spectrum of a set of flutings in the ultra-violet.† The conclusion that these flutings were due to the vapour of carbon, and not to any compound of carbon, was founded upon experiments similar to those employed in the researches of Attfield and Watts, who showed that the other almost exactly similar sets of flutings in the visible part of the spectrum were seen when several different compounds of carbon were exposed to the action of heat and electricity. In my photographs the ultra-violet flutings appeared under conditions in which carbon was the only constant, and it seemed therefore reasonable to assume that the flutings were due to carbon itself, and not to any compound of carbon.

Professors Liveing and Dewar have recently on several occasions called this result in question. Professor Dewar, in a paper received by the Royal Society on January 8, 1880, writes as follows:—

"The almost impossible problem of eliminating hydrogen from masses of carbon, such as can be employed in experiments of this kind, prove conclusively that the inference drawn by Mr. Lockyer as to the elementary character of the so-called carbon spectrum from an examination of the arc in dry chlorine, cannot be regarded as satisfactory, *seeing that undoubtedly hydrogen was present in the carbon*‡ used as the poles."

Subsequently, in a paper received by the Royal Society on February 2, Messrs. Liveing and Dewar wrote as follows:—

* "Proc. Roy. Soc.," vol. 27, p. 308.

† The approximate wave-length of the brightest member on the least refrangible edge is 3881·0.

‡ The italics are mine.—J. N. L.

“Mr. Lockyer (‘Proc. Roy. Soc.,’ vol. 27, p. 308) has recently* obtained a photograph of the arc in chlorine, which shows the series of fluted bands in the ultra-violet, on the strength of which he throws over the conclusion of Ångström and Thalèn, and draws inferences as to the existence of carbon vapour above the chromosphere in the coronal atmosphere of the sun, which, if true, would be contrary to all we know of the properties of carbon. We cannot help thinking that *these bands were due to the presence of a small quantity of nitrogen.*” †

It will be seen that on January 8 Mr. Dewar alone attributed the flutings to hydrocarbon, while on February 2 Mr. Dewar, associated with Mr. Liveing, attributed them to a nitrocarbon.

In the latter paper Messrs. Liveing and Dewar published some experiments on the spectra of various carbon compounds, and from their observations they have drawn the conclusion that the set of flutings which I have shown to be reversed in the solar spectrum is really due to cyanogen, and that certain other sets of flutings shown by Attfield and Watts to be due to carbon are really due to hydrocarbon.

As Messrs. Liveing and Dewar do not controvert the very definite conclusions arrived at by Attfield, Morren, Watts, and others, I can only presume that they have taken for granted that the experimental work performed by these men was tainted by the presence of impurities, and that it was impossible to avoid them. I have therefore thought it desirable to go over the ground again, modifying the experimental method so as to demonstrate the absence of impurities. Indeed, I have started upon a somewhat lengthy research, and have taken a large number of photographs under various conditions, so that to reduce them all will be a work of time. I beg permission, therefore, in the meantime, to submit to the notice of the Society an experiment with a tube containing CCl_4 , which, I think, establishes the conclusions arrived at by prior investigators. And I may add that it is the more important to settle the question, as Messrs. Liveing and Dewar have already based upon their conclusions theoretical views of a kind which appear to me calculated to mislead, and which I consider to have long been shown to be erroneous.

As my results, to which I now draw attention, simply endorse former work, it is important to state that former work somewhat at length and in the words of the authors.

The prior work of Attfield (in 1862) will be gathered from the following extract from his paper (“Phil. Trans.,” vol. 152, p. 221 *et seq.*):—

“On recently reading Swan’s paper by the light that Professors Bunsen and Kirchhoff have thrown on the subject, I came to the conclusion that these bands must be due to incandescent carbon vapour;

* That is, in 1878.—J. N. L.

† The italics are mine.—J. N. L.

that, if so, they must be absent from flames in which carbon is absent, and present in flames in which carbon is present; that they must be observable equally in the flames of the oxide, sulphide, and nitride as in that of the hydride of carbon; and, finally, that they must be present whether the incandescence be produced by the chemical force, as in burning jets of the gases in the open air, or by the electric force, as when hermetically sealed tubes of the gases are exposed to the discharge of a powerful induction coil. . . .

"To establish the absolute identity of the hydro- and nitro-carbon spectra, excluding of course the lines due to nitrogen, they were simultaneously brought into the field of the spectroscope: one occupying the upper, and the other the lower half of the field.

"This was readily effected after fixing the small prism, usually supplied with spectroscopes, over half of the narrow slit at the further end of the object-tube of the instrument. The light from the oxyhydrocarbon flame was now directed up the axis of the tube by reflection from the little prism, while that from the oxynitrocarbon flame passed directly through the uncovered half of the slit. A glance through the eye-tube was sufficient to show that the characteristic lines of the hydrocarbon spectrum were perfectly continued in the nitrocarbon spectrum. A similar arrangement of apparatus, in which the hydrocarbon light was replaced by that of pure nitrogen, showed that the remaining lines of the nitrocarbon spectrum were identical with those of the nitrogen spectrum. In this last experiment the source of the pure nitrogen light was the electric discharge through the rarefied gas.

"The above experiment certainly seemed to go far towards proving the spectrum in question to be that of the element carbon. Nevertheless, the ignition of the gases having been effected in air, it was conceivable that hydrogen, nitrogen, or oxygen had influenced the phenomena. To eliminate this possible source of error, the experiments were repeated out of contact with air. A thin glass tube 1 inch in diameter and 3 inches long, with platinum wires fused into its sides, and its ends prolonged by glass quills having a capillary bore, was filled with pure dry cyanogen, and the greater portion of this gas then removed by a good air-pump. Another tube was similarly prepared with olefiant gas. The platinum wires in these tubes were then so connected with each other that the electric discharge from a powerful induction-coil could pass through both at the same time. On now observing the spectra of these two lights in the simultaneous manner previously described, the characteristic lines of the hydrocarbon spectrum were found to be rigidly continued in that of the nitrocarbon. Moreover, by the same method of simultaneous observation, the spectrum of each of these electric flames, as they may be termed, was compared with the corresponding chemical flames, that is, with

the oxyhydrocarbon and oxynitrocarbon jets of gas burning in air. The characteristic lines were present in every case. Lastly, by similar inter-observation a few other lines in the electric spectrum of the hydrocarbon were proved to be due to the presence of hydrogen, and several others in the electric spectrum of the nitrocarbon to be caused by the presence of nitrogen. . . .

“The spectrum under investigation having then been obtained in one case when only carbon and hydrogen were present, and in another when all elements but carbon and nitrogen were absent, furnishes, to my mind, sufficient evidence that the spectrum is that of carbon.

“But an interesting confirmation of the conclusion just stated is found in the fact that the same spectrum is obtained when no other elements but carbon and oxygen are present, and also when carbon and sulphur are the only elements under examination. And first with regard to carbon and oxygen. Carbonic oxide burned in air gives a flame possessing a continuous spectrum. A mixture of carbonic oxide and oxygen burned from a platinum-tipped safety-jet also gives a more or less continuous spectrum, but the light of the spectrum has a tendency to group itself in ill-defined ridges. Carbonic oxide, however, ignited by the electric discharge in a semi-vacuous tube, gives a bright sharp spectrum. This spectrum was proved, by the simultaneous method of observation, to be that of carbon plus the spectrum of oxygen. With regard to carbon and sulphur almost the same remarks may be made. Bisulphide of carbon vapour burns in air with a bluish flame. Its spectrum is continuous. Mixed with oxygen and burned at the safety-jet, its flame still gives a continuous spectrum, though more distinctly furrowed than in the case of carbonic oxide; but when ignited by the electric current its spectrum is well defined, and is that of carbon plus the sulphur. That is to say, it is the spectrum of carbon plus the spectrum that is obtained from vapour of sulphur when ignited by the electric discharge in an otherwise vacuous tube.

“Having thus demonstrated that dissimilar compounds containing carbon emit, when sufficiently ignited, similar rays of light, I come to the conclusion that those rays are characteristic of ignited carbon vapour, and that the phenomenon they give rise to on being refracted by a prism is the spectrum of carbon.”

The only reference to this admirable work, in which vacuum tubes and the electric discharge were largely employed, which I can find in Messrs. Dewar and Liveing's paper is the following:—“The spectrum of hydrocarbon *burning in air** has been . . . described . . . by Attfield.”

In 1865 Morren wrote: †—

“A la réception de cet intéressant et substantiel Mémoire, j'avoue

* The italics are mine.—J. N. L.

† “Annales de Chemie et de Physique,” 4 série, tome iv, pp. 309, 312.

que je ne regardai pas d'abord comme fondée l'assertion de M. Attfield. . . .

"Je me suis donc mis au travail avec la pensée préconçue de combattre l'assertion émise par le savant Anglais; mais pas du tout, il résulte au contraire des expériences auxquelles je me suis livré que M. Attfield a raison, et que c'est bien la vapeur du carbone qui donne la spectre indiqué plus haut. . . .

"Si on fait brûler le cyanogène au moyen du chalumeau à deux courants, en faisant arriver au centre de la flamme du cyanogène un courant d'oxygène très-pur (cette condition est indispensable) on voit se produire un des plus beaux effets de combustion possible, et cette expérience est certainement une des plus magnifiques qu'on puisse réaliser sur la combustion des gaz. Il se produit, au milieu de la flamme *rosé-violâtre* du cyanogène, une boule d'un blanc vert ébouissant qui rappelle la lumière électrique produite par le courant de la pile entre deux charbons de cornue. Si le spectroscope est dirigé sur cette brillante lumière, on aperçoit, avec une splendeur merveilleuse, le même spectre de la partie bleue des flammes hydrocarburées. Ainsi donc c'est du charbon seul, mais à l'état de vapeur, qui forme cette boule brillante qui plus loin, par son union avec l'oxygène, va passer à l'état d'acid carbonique. Du reste ce spectre n'est pas seul; avec lui on voit, mais très-effacé, le spectre spécial du cyanogène, et celui-ci tend de plus en plus à disparaître à mesure que l'oxygène arrive avec plus d'abondance et brûle de mieux en mieux le cyanogène. Quant au spectre de l'azote, on ne l'aperçoit pas dans cette vive lumière. Le magnifique éclat de ce beau spectre, le plus beau qu'il m'ait été donné de voir, permet de bien comprendre l'aspect creusé et ombré avec une teinte croissante qu'on remarque dans les parties qui n'ont pas de raies brillantes, et même entre ces raies."

Four years later Dr. Watts took up the question, and in 1869 his work was thus summarised by himself: *—

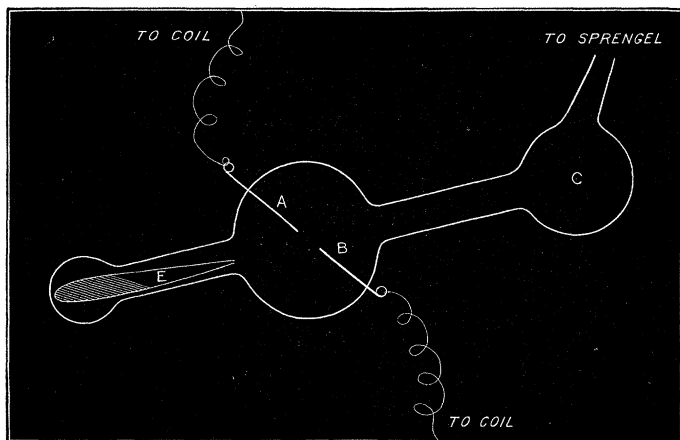
"This spectrum (that consisting of the flutings in question) may be obtained from the flame of any hydrocarbon, though in many cases, owing to the faintness of the spectrum, only some of the groups can be recognised. In the flame of an ordinary Bunsen burner δ and ϵ are easily seen, γ and f are much fainter, and the red group cannot be detected.

"This spectrum is proved to be that of carbon, inasmuch as it can be obtained alike from compounds of carbon with *hydrogen*, with *nitrogen*, with *oxygen*, with *sulphur*, and with *chlorine*. I have obtained it, namely, from each of the following compounds:—Olefiant gas, cyanogen, carbonic oxide, naphthalin, carbonic disulphide, carbonic tetrachloride, amylic alcohol, and marsh-gas."

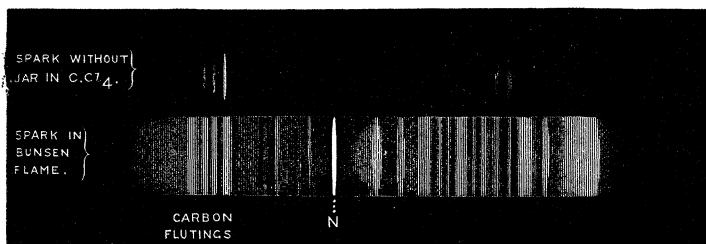
* "Phil. Mag.," October, 1869.

I now come to my own experiments.

The tube to which I have already referred is shown in the diagram : A and B are platinum wires for passing the spark inside the tube ; E is a small tube into which carbon tetrachloride was introduced ; it was drawn out to a long narrow orifice to prevent the rapid evaporation of the liquid during the exhaustion of the tube. The tube was bent upwards and a bulb blown at c in order that the spark might be



examined with the tube end-on, as it is found that after the spark has passed for some time a deposit is formed on the sides of the bulb immediately surrounding the platinum, thus obstructing the light. After a vacuum had been obtained the tube was allowed to remain on the Sprengel for a long time, in order that the last traces of air might be expelled by the slow evaporation of the liquid.



The carbon tetrachloride was prepared by Dr. Hodgkinson, who very kindly supplied me with sufficient for my experiments.

On passing the spark without the jar in this tube, the spectrum observed consists of those sets of flutings which, according to Messrs.

Liveing and Dewar, are due to hydrocarbon, and the set of flutings which is reversed in the sun, and ascribed by Messrs. Liveing and Dewar to cyanogen, also appear in a photograph of the violet end of the spectrum. On connecting a Leyden jar with the coil and then passing the spark the flutings almost entirely vanish and the line spectra of chlorine and carbon take the place of the flutings without either a line of hydrogen or a line of nitrogen being visible.

As a long experience has taught me that these tubes often leak slightly at the platitudes after they are detached from the pump, I took the occasion afforded by a visit of Dr. Schuster to my laboratory while the experiments were being made to get my observations confirmed. He has been good enough to write me the following letter, and to allow me to give it here:

“*March 21.*

“MY DEAR LOCKYER,—The following is an account of the experiment which I saw performed in your laboratory on Monday, March 15:—

“A tube containing carbon tetrachloride was attached to the Sprengel pump. As exhaustion proceeded the air was gradually displaced by the vapour of the tetrachloride. The electrodes were a few millimetres apart. If the spark was taken without a condenser in the vapour the well-known carbon bands first discovered by Swan in the spectrum of a candle were seen with great brilliancy; I also saw the blue band which you said was identical in position with one of the blue bands seen in the flame of cyanogen or in the spectrum of the electric arc. When the condenser and air-break were introduced this spectrum gave way to a line spectrum in which I could recognise the lines of chlorine. *The lines of nitrogen were absent, not a trace of the principal double line in the green being seen.* The hydrogen line $H\alpha(C)$ was faintly visible when I first observed the spectrum, but it got gradually weaker and *finally disappeared altogether.* *When this line was no longer visible the condenser was taken out of circuit again, and the same carbon bands were seen as before.* These bands, therefore, show themselves with great brilliancy when a strong and powerful spark does not reveal the presence either of hydrogen or nitrogen.

“(Signed) ARTHUR SCHUSTER.”

This result, which entirely endorses the work of Attfield and Watts, has been controlled by many other experiments. I have also repeated Morren's experiment and confirmed it, and I have also found that the undoubted spectrum of cyanogen is visible neither in the electric arc nor in the surrounding flame.

I hope to show in the complete paper that the various difficulties which have always been acknowledged to attend observations of this substance may in all probability be due to the fact that the sets of carbon flutings represent different molecular groupings of carbon, in

addition to that or those which give us the line spectrum, and that the tension of the current used now brings one set of flutings into prominence, and now another.

I have so often taken occasion to refer with admiration to the work of Ångström and Thalèn that I shall not be misunderstood when I say that their conclusions, to which such prominence is given, and on which such great stress is laid, by Messrs. Liveing and Dewar, rests more upon a theory which has been shown to be false since the labours commenced and analogy than upon experiment.

Their work, undertaken at a time when the existence of so-called "double spectra" was not established upon the firm basis that it has now, and when there was no idea that the spectrum recorded for us the results of successive dissociations, gave the benefit of the doubt in favour of flutings being due to compounds, and it was thought less improbable that cyanogen or acetylene should have two spectra than that carbon or hydrogen should possess them.

These views were accepted by myself until years of work and experience had shown them to be untenable, and later researches have thrown doubt upon the view that the fluted spectra of aluminium and magnesium are entirely due to the oxides of those metals instead of to the metals themselves—and this is the very basis of the analogy which Ångström and Thalèn employed.

From what I have shown it will be clear that the consequences drawn in the following paragraphs* by Messrs. Liveing and Dewar from the assumed hydrogen-carbon bands are entirely invalid.

"The similarity in the character of the magnesium-hydrogen spectrum, which we have described, to the green bands of the hydrocarbons is very striking. We have similar bright maxima of light, succeeded by long drawn-out series of fine lines, decreasing in intensity towards the more refrangible side. This peculiarity, common to both, impels the belief that it is a consequence of a similarity of constitution in the two cases, and that magnesium forms with hydrogen a compound analogous to acetylene. In this connexion the very simple relation (2 : 1) between the atomic weights of magnesium and carbon is worthy of note, as well as the power which magnesium has, in common with carbon as it now appears, of combining directly with nitrogen. We may with some reason expect to find a magnesium-nitrogen spectrum.

"The interest attaching to the question of the constitution of comets, especially since the discovery by Huggins that the spectra of various comets are all identical with the hydrocarbon spectrum, naturally leads to some speculation in connexion with conclusions to

* Paper read February 2, 1880.

which our experiments point. Provided we admit that materials of the comet contain ready formed hydrocarbons, and that oxidation may take place, then the acetylene spectrum might be produced at comparatively low temperatures without any trace of the cyanogen spectrum or of metallic lines. If, on the other hand, we assume only the presence of uncombined carbon and hydrogen, we know that the acetylene spectrum can only be produced at a very high temperature, and if nitrogen were also present that we should have the cyanogen spectrum as well. Either, then, the first supposition is the true one, not disproving the presence of nitrogen, or else the atmosphere which the comet meets is hydrogen only, and contains no nitrogen."

II. "On the Diurnal Variation in the Amount of Carbon Dioxide in the Air." By GEORGE FREDERICK ARMSTRONG, M.A., F.G.S., C.E., Professor of Engineering in the Yorkshire College, Leeds. Communicated by Professor THORPE, F.R.S. Received April 12, 1880.

Although a large share of attention has been given to the elucidation of the causes which influence the amount of carbonic acid present in the atmosphere during the day, no systematic observations with reference to the relative quantities present in the air of the land during the day and the night appear to have been undertaken since the well-known experiments of the younger De Saussure at Chambeisy,* upwards of 50 years ago (1826-30), and a similar set by Boussingault at Paris,† a few years later, until M. Truchot‡ took up the question in 1873. But the results thus obtained cannot be said to be altogether satisfactory.

On the other hand, the question as to the existence of a diurnal variation in the amount of carbonic acid in sea-air may be said to have been fully worked out and set at rest by the careful and extensive set of observations made some years ago by Dr. Thorpe§ on the air of the Irish Sea and Atlantic Ocean. His results went to show that no appreciable diurnal difference exists.

As regards a diurnal variation in the case of land-air, the results of De Saussure are somewhat contradictory; and latterly, what he himself considered as "one of the most remarkable results" in the whole range of his inquiries—the discovery of a distinct diurnal variation in the amount of carbonic acid—has been regarded as but very imperfectly established.

De Saussure published his first set of results which were deduced

* "Ann. de Chim. et de Phys.," vols. xxxviii (1828) and xlv (1830).

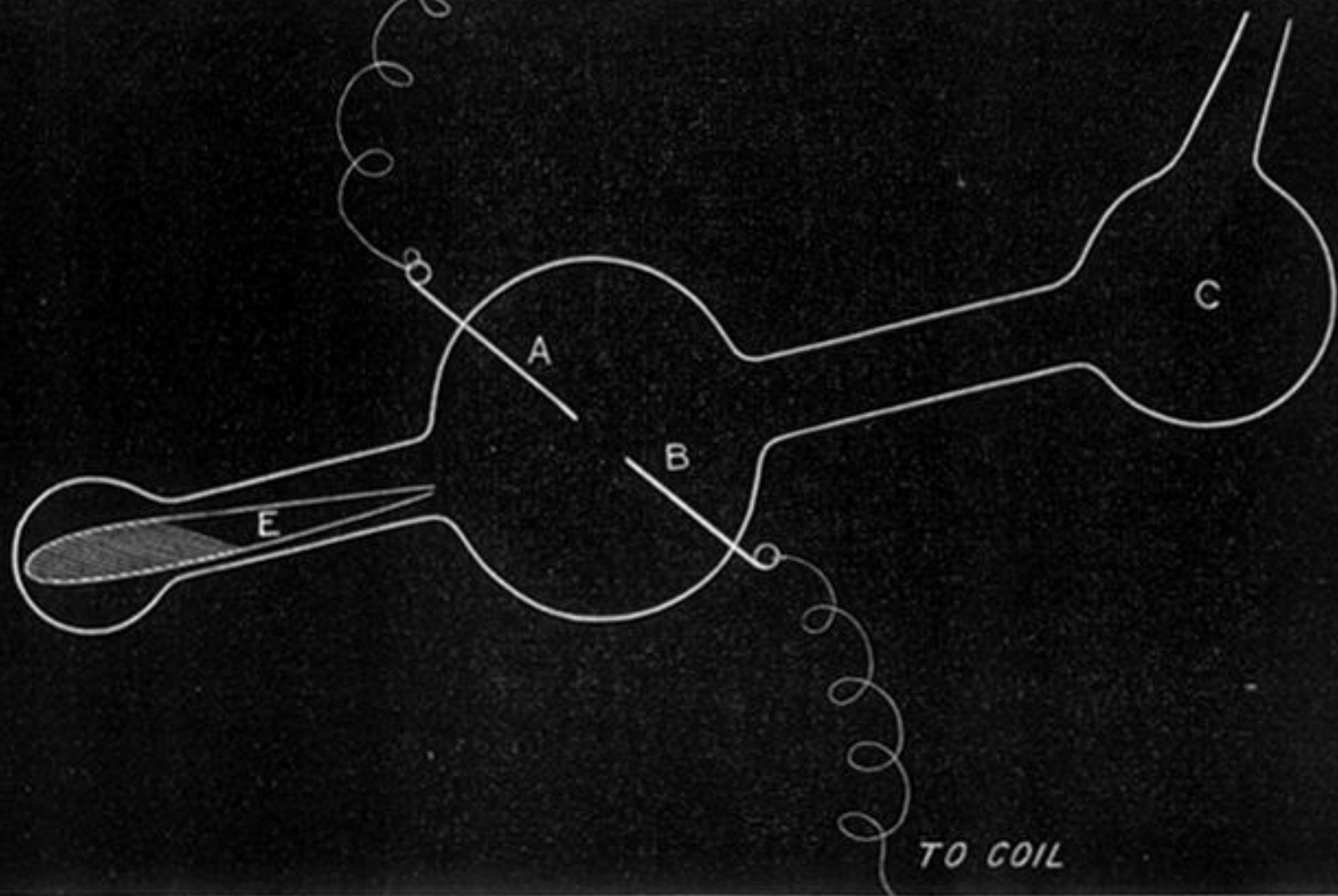
† "Ann. de Chim. et de Phys.," [3], 10 (1844).

‡ "Compt. Rend.," 77, 675.

§ "Journ. Chem. Soc.," [12], v. 189.

TO COIL

TO SPRENGEL

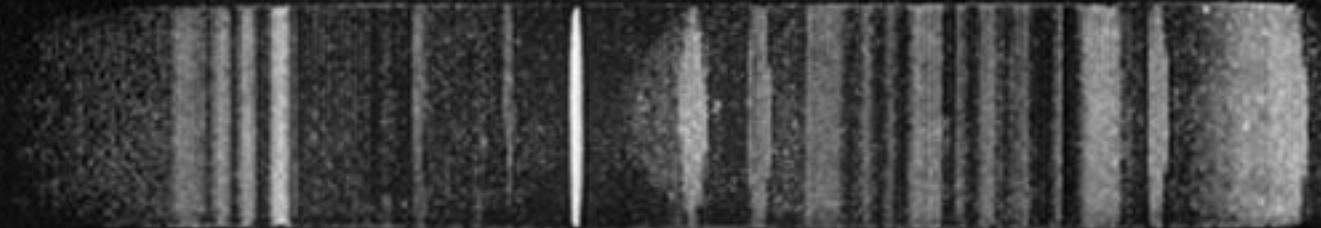


SPARK WITHOUT
JAR IN C_2F_4 .

SPARK IN
BUNSEN
FLAME.

CARBON
FLUTINGS

N

A horizontal photograph showing two spectra side-by-side. The top spectrum, labeled 'SPARK WITHOUT JAR IN C2F4', shows a few sharp, isolated vertical lines. The bottom spectrum, labeled 'SPARK IN BUNSEN FLAME', shows a much denser series of vertical lines. A central vertical line in the bottom spectrum is labeled 'N' with three dots above it. The label 'CARBON FLUTINGS' is positioned below the left side of the bottom spectrum.